PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C03C 3/087, 3/095, 4/08
B32B 17/10, 27/42

A1

(11) International Publication Number: WO 91/07356

(43) International Publication Date: 30 May 1991 (30.05.91)

(21) International Application Number: PCT/US90/06587

(22) International Filing Date: 12 November 1990 (12.11.90)

(30) Priority data:

438,538	16 November 1989 (16.11.89)	US
542,207	21 June 1990 (21.06.90)	US
575,127	30 August 1990 (30.08.90)	US

(71) Applicant: LIBBEY-OWENS-FORD CO. [US/US]; 811 Madison Avenue, Toledo, OH 43695 (US).

(72) Inventor: CHENG, J., Joseph ; 309 W. South Boundary, Perrysburg, OH 43551 (US).

(74) Agent: OBERLIN, Phillip, S.; Marshall & Melhorn, Four SeaGate - 8th Floor, Toledo, OH 43604 (US).

(81) Designated States: AT (European patent), AU, BE (European patent), BG, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, RO, SE (European patent), SU.

Published
With international search report.

(54) Title: INFRARED AND ULTRAVIOLET RADIATION ABSORBING GREEN GLASS COMPOSITION

(57) Abstract

Green-colored, infrared energy and ultraviolet radiation absorbing glass compositions comprise conventional soda-lime-silica float glass ingredients, a high concentration of moderately reduced iron, and ceric oxide. The resultant glass exhibits an Illuminant A visible light transmittance greater than 70 %, a total solar energy transmittance less than about 46 %, and an ultraviolet radiation transmittance less than about 38 %, at glass thicknesses in the range of 3 mm to 5 mm. Optionally, a portion of the ceric oxide can be replaced with a predetermined quantity of titanium oxide. Further the glass may be used in an automobile glazing unit comprising two sheets of the glass integrally adhered together through an interposed layer of transparent resinous material such as polyvinyl butyryl.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	SD	Sudan
CF	Central African Republic	KP	Democratic People's Republic of Korea	SE	Sweden
CG	Congo			SN	Senegal
CH	Switzerland	KR	Republic of Korea	SU	Soviet Union
CI	Côte d'Ivoire	LI	Liechtenstein	TD	Chad
CM	Cameroon	LK	Sri Lanka	TG	Togo
DE	Germany	LU	Luxembourg	US	United States of America
DK	Denmark	MC	Monaco		
ES	Spain	MG	Madagascar		

Description

INFRARED AND ULTRAVIOLET RADIATION ABSORBING GREEN GLASS COMPOSITION

Field of the Invention

The present invention relates generally to infrared and ultraviolet radiation absorbing green glass compositions, and more specifically to green glass compositions having a particular combination of energy absorption and light transmittance properties. The preferred glass has a narrowly defined dominant wavelength and color purity. The present invention is particularly useful for producing automotive and architectural glazings, wherein high visible light transmittances and low total solar energy and ultraviolet radiation transmittances are desired.

Background of the Invention

It is generally known to manufacture infrared radiation absorbing soda-lime-silica glass by the incorporation therein of iron. The iron is generally present in the glass as both ferrous oxide (FeO) and ferric oxide (Fe_2O_3). The balance between ferrous and ferric oxide has a direct and material effect on the color and transmittance properties of the glass. As the ferrous oxide content is increased (as a result of chemically reducing ferric oxide), the infrared absorption increases and the ultraviolet absorption decreases. The shift toward a higher concentration of FeO in relation to the Fe_2O_3 also causes a change in the color of the glass from a yellow or yellow-green to a darker green or blue-green, which reduces the visible transmittance of the glass. Therefore, in order to obtain greater infrared absorption in glass without sacrificing visual transmittance, it has been deemed necessary in the prior art to produce glass with a low total iron content which is highly reduced from Fe_2O_3 to FeO. A low total iron content glass is generally regarded as one produced from a batch composition

having less than about .70 to .75% by weight iron calculated as Fe_2O_3. As an example, U.S. Patent No. 3,652,303 discloses an infrared absorbing blue soda-lime-silica glass composition, having a visible light transmittance greater than 70% at one quarter inch thickness, wherein at least 80% of the total iron in the glass is maintained in the ferrous state by the inclusion of a reducing quantity of tin metal or stannous chloride in the melt.

Many glass compositions additionally contain cerium for the purpose of providing ultraviolet absorption. For example, U.S. Patent No. 1,414,715 discloses the addition of 3% to 6% by weight of ceric oxide to prepare a non-iron-containing glass composition having a flesh tint. The patent additionally teaches that ceric oxide reduces the visible light transmittance of the glass.

U.S. Patent No. 1,637,439 discloses the use of 5% to 10% by weight of ceric oxide as an ultraviolet absorber in dark blue glass compositions. The glass, which is useful for example for observing the operation of an open-hearth furnace, is made dark blue by the addition of 0.1% to 0.5% by weight of cobalt oxide. The high concentration of ceric oxide absorbs virtually all of the ultraviolet radiation which would otherwise pass through the eye protecting glass. Clearly, such a glass composition has a low visible light transmittance, and would not be useful for automotive or architectural glazings.

U.S. Patent No. 1,936,231 discloses a colorless glass, wherein ferric oxide is added as an ultraviolet cut-off agent in quantities so small that the resultant glass retains its high visible light transmittance. The suggested total iron content is approximately 0.35% by weight. The patent further discloses that cerium compounds may be added, as ultraviolet radiation cut-off agents, to low total iron containing glass compositions. Thus, the resultant glass compositions retain their colorless appearance and high visible light transmittance properties.

U.S. Patent No. 2,524,719 discloses a rose colored glass composition, wherein iron is added to the glass batch as an infrared energy absorber, and selenium is added as an ultraviolet radiation absorber. It is suggested that ceric oxide may be included, at an amount in excess of 3% by weight, to assist the selenium in the absorption of ultraviolet radiation.

U.S. Patent No. 2,860,059 discloses an ultraviolet absorbing glass composition, having a low total iron concentration, which is described as superior in visible light transmittance to the greenish-blue glasses generally used in automotive and architectural glazings. The maximum iron content is 0.6% by weight, in order for the glass to maintain its colorless appearance and high visible light transmittance. Titanium dioxide, and up to 0.5% by weight ceric oxide, are added to the glass for the purpose of providing ultraviolet radiation absorption.

U.S. Patent No. 2,444,976 discloses a golden color glass particularly adapted for glazing aircraft having an exceptionally low transmittance in the ultraviolet and a high transmittance in the visible. The glass contains iron oxide as a heat absorbing component together with large amounts of both cerium oxide (1.5% to 3%) and titanium oxide (6% to 9%).

Finally, U.S. Patent No. 4,792,536 discloses a process for producing an infrared energy absorbing glass, containing a low total iron concentration which is highly reduced to FeO. It is further disclosed that the infrared energy absorption can be increased by including greater amounts of total iron in the glass composition, but states that the visible light transmittance would thereby be reduced below levels considered adequate for automotive glazings. The disclosed process utilizes a two stage melting and refining operation, which provides highly reducing conditions so as to increase the amount of iron in the ferrous state for a given low total iron concentration of from 0.45% to 0.65% by weight. The patent teaches that the iron must be at least

35% reduced to FeO. Most preferably, greater than 50% of the total iron content must be reduced to the ferrous state. It is further disclosed that 0.25% to 0.5% by weight of ceric oxide may be added to low total concentration, highly reduced iron containing glass compositions, for the purpose of absorbing ultraviolet radiation. It is disclosed that higher concentrations of ceric oxide are to be avoided, as they would compromise the overall transmittance properties of the glass. As an example of the glass which may be produced by the process taught in U.S. Patent No. 4,792,536, Composition No. 11 discloses a low total iron containing glass, which is 30% reduced to FeO, and contains 1% ceric oxide. At a thickness of 4 mm, the total solar energy transmittance is about 52%, and the ultraviolet radiation transmittance is about 37%. The relatively high total solar energy transmittance value results from the low total iron concentration, while the relatively high ultraviolet radiation transmittance value is caused by the low concentration of Fe_2O_3, a large portion of which has been reduced to FeO.

It would be desirable to produce a green-colored glass, utilizing conventional float glass technology, for use in automotive and architectural glazings, having a high Illuminant A visible light transmittance of at least 70%, a low total solar energy transmittance of less than about 46%, and a low ultraviolet radiation transmittance of less than about 38%, at nominal glass thicknesses in the range of 3 mm to 5 mm *. A green glass composition having these outstanding transmittance properties can not be produced utilizing the low total concentration, highly reduced iron

* It should be understood that by this recitation of glass thickness is meant total glass thickness, and the glazing unit comprising same may be composed of a single glass sheet or two or more glass sheets, the total thickness of which is in the indicated range.

containing glass compositions employing ceric oxide as disclosed in the prior art. Moreover, the use of a high total iron containing glass for this purpose is contrary to the teachings of the prior art.

It must be noted that the prior art referred to hereinabove has been collected and examined only in light of the present invention as a guide. It is not to be inferred that such diverse art would otherwise be assembled absent the motivation provided by the present invention.

Summary of the Invention

In accordance with the present invention, a green glass composition, having an Illuminant A visible light transmittance value of at least 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 38% and preferably not greater than approximately 34%, at nominal glass thicknesses of 3 to 5 mm, has surprisingly been discovered.* The composition comprises a soda-lime-silica glass including as essential ingredients from about 0.51 to about 0.96 weight percent Fe_2O_3, from about 0.15 to about 0.33 weight percent FeO, and from about 0.2 to about 1.4 weight percent CeO_2. Alternatively, the amount of CeO_2 may be reduced by the inclusion of from about 0.02 to about 0.85 weight percent TiO_2. Percentages of TiO_2 below about .02 weight percent are normally present as trace amounts in soda-lime-silica glasses. These glasses have an Illuminant C dominant wavelength from about 498 to about 525 nanometers, preferably from 498 to 519 nanometers, and a color purity from about 2% to about 4% preferably from about 2% to about 3%. They are

---

* Radiation transmittance results are based upon the following wavelength ranges:

Ultraviolet	300-400	nanometers
Visible	400-770	nanometers
Total Solar	300-2130	nanometers

produced from batch compositions having a total iron concentration, expressed as Fe_2O_3, above about 0.7%. *

The glass compositions of the present invention are particularly suited for the production of infrared energy and ultraviolet radiation absorbing green glass, for automotive and architectural glazings. Thus, glass sheets of this composition may be heat strengthened or tempered, or alternately annealed and laminated together through an interposed transparent resinous layer, for example composed of polyvinyl butyral, and employed, for example, as a windshield. Generally, the glass sheets for windshield use are of a thickness in the range of from about 1.7 mm to about 2.5 mm, while those tempered and used as sidelights or backlights are in the range of about 3 mm to about 5 mm thick.

Unless otherwise noted, the term percent (%) as used herein and in the appended claims, means percent (%) by weight. Wavelength dispersive X-ray fluorescence was used to determine the weight percents of CeO_2, TiO_2, and total iron expressed as Fe_2O_3. Percent reduction of total iron was

---

* It is common in the glass industry to refer to the total iron contained in a glass composition or batch as "total iron expressed as Fe_2O_3". When a glass batch is melted, however, some of this amount of total iron is reduced to FeO, while the rest remains Fe_2O_3. For this reason, it shall be understood that by "Fe_2O_3", as used herein and in the appended claims, is meant weight percent ferric oxide in the glass composition after reduction. By "total iron expressed as Fe_2O_3" is meant the total weight of iron contained in the glass batch before reduction. Further, when reduced to FeO, Fe_2O_3 will produce not only FeO, but oxygen gas. This loss of oxygen will decrease the combined weight of the two iron compounds. Therefore, the combined weight of FeO and Fe_2O_3 contained in a resulting glass composition will be less than the batch weight of the total iron expressed as Fe_2O_3.

determined by first measuring the radiant transmission of a sample at a wavelength of 1060 nanometers, using a spectrophotometer. The 1060 nm transmission value was then used to calculate optical density, using the following formula:

$$\text{Optical density} = \text{Log}_{10} \frac{100}{T} \quad (T = \text{transmission at 1060 nm}).$$

The optical density was then used to calculate the percent reduction:

$$\text{percent reduction} = \frac{(110)\text{x}(\text{optical density})}{(\text{Glass thickness in mm})\text{x}(\text{wt\% total } Fe_2O_3)}$$

Detailed Description of the Preferred Embodiment

For use as an automotive windshield, infrared energy and ultraviolet radiation absorbing glass must meet federal specifications which require an Illuminant A visible light transmittance greater than 70%. The thinner glasses used in modern automobiles have made it easier to achieve the 70% Illuminant A standard, but have also resulted in increased infrared energy and ultraviolet radiation transmittances. Consequently, automobile manufacturers have been forced to compensate for greater heat loads by appropriately sizing air conditioning equipment, and are compelled to include more ultraviolet radiation stabilizers in fabrics and interior plastic components in order to prevent their degradation.

The green glass compositions of the present invention, when fabricated to a total glass thickness of about 3 mm to 5 mm, can exhibit an Illuminant A visible light transmittance value of at least 70%, and provide combined infrared energy and ultraviolet radiation transmittance values substantially lower than the compositions disclosed in the prior art. The total solar energy transmittance of the compositions of the present invention, at selected glass thicknesses in the range of 3 mm to 5 mm, is less than about 46%. Preferably, the total solar energy transmittance in these thicknesses is less than about 45%. Total solar energy transmittance is a

measure of the solar energy transmittance over all solar energy wavelengths. It is an integrated term covering the area under the transmittance versus wavelength curve for visible, infrared and ultraviolet energy wavelengths.

The ultraviolet radiation transmittance of the compositions of the present invention is less than about 38%, at selected glass thicknesses in the range of 3 mm to 5 mm, and generally not more than about 34%. The ultraviolet radiation transmittance value is an integrated term representing the area under the transmittance versus wavelength curve for wavelengths between 300 and 400 nanometers. The ultraviolet radiation transmittance values for glass compositions of the present inventions were calculated by integrating the Perry Moon air mass 2 solar spectral energy distribution* between 300 and 400 nm, and ratioing the attenuated energy transmitted by the sample over that same spectral region.

Suitable batch materials according to the present invention, which are compounded by conventional glass batch ingredient mixing devices, include sand, limestone, dolomite, soda ash, salt cake or gypsum, rouge, carbon, and a cerium compound such as ceric oxide or cerium carbonate, and optionally a titanium compound such as titanium dioxide. These materials are conveniently melted together in a conventional glass making furnace, to form a green-colored infrared energy and ultraviolet radiation absorbing glass composition, which thereafter may be continuously cast onto the molten metal bath in a float glass process. The flat glass thus produced may be formed into architectural glazings, or cut and formed, such as for example by press bending, into automotive glazings.

---

* From "Proposed Standard Solar-Radiation Curves for Engineering Use", Perry Moon, M.I.T., Journal of the Franklin Institute, No. 230, pp. 583-617 (1940).

The composition of the resultant soda-lime-silica glass comprises:

A) from about 65 to about 75 weight percent SiO_2;

B) from about 10 to about 15 weight percent Na_2O;

C) from 0 to about 4 weight percent K_2O;

D) from about 1 to about 5 weight percent MgO;

E) from about 5 to about 15 weight percent CaO;

F) from 0 to about 3 weight percent Al_2O_3;

G) from about 0.51 to about 0.96 weight percent Fe_2O_3;

H) from about 0.15 to about 0.33 weight percent FeO; and

I) from about 0.2 to about 1.4 weight percent CeO_2.

Preferably, the resultant glass composition consists essentially of:

A) from about 70 to about 73 weight percent SiO_2;

B) from about 12 to about 14 weight percent Na_2O;

C) from 0 to about 1 weight percent K_2O;

D) from about 3 to about 4 weight percent MgO;

E) from about 6 to about 10 weight percent CaO;

F) from 0 to about 2 weight percent Al_2O_3;

G) from about 0.51 to about 0.96 weight percent Fe_2O_3;

H) from about 0.15 to about 0.33 weight percent FeO; and

I) from about 0.2 to about 1.4 weight percent CeO_2.

Alternatively, the quantity of ceric oxide in the glass may be reduced by the inclusion therein of titanium dioxide. In order to maintain the desired ranges of transmittance, dominant wavelength, and color purity described hereinabove, when substituting titanium dioxide for ceric oxide in the glass, the weight percent of total iron expressed as Fe_2O_3 must be reduced, and the percent reduction to FeO must be increased. This results in a glass comprising:

A) from about 65 to about 75 weight percent SiO_2;

B) from about 10 to about 15 weight percent Na_2O;

C) from 0 to about 4 weight percent K_2O;

D) from about 1 to about 5 weight percent MgO;

E) from about 5 to about 15 weight percent CaO;

F) from 0 to about 3 weight percent Al_2O_3;

G) from about 0.5 (.48) to about 0.9 (.92) weight percent Fe_2O_3;

H) from about 0.15 to about 0.33 weight percent FeO;

I) from about 0.1 to about 1.36 weight percent CeO_2; and

J) from about 0.02 to about 0.85 weight percent TiO_2.

It shall be noted that, at low quantities of TiO_2 inclusion, each weight percent of TiO_2 must replace two weight percent of CeO_2 to maintain the glass properties described hereinabove. As the level of TiO_2 increases, however, the effect of TiO_2 addition lessens slightly. For example, a composition initially containing 1.0 weight percent CeO_2 and no added TiO_2 will require about .3 weight percent TiO_2 to replace about .5 weight percent CeO_2 and still maintain glass properties (thus at higher quantities of TiO_2 substitution, each weight percent TiO_2 will replace about 1.5 weight percent CeO_2). Preferably, the glass composition employing titanium dioxide consists essentially of:

A) from about 70 to about 73 weight percent SiO_2;

B) from about 12 to about 14 weight percent Na_2O;

C) from 0 to about 1 weight percent K_2O;

D) from about 3 to about 4 weight percent MgO;

E) from about 6 to about 10 weight percent CaO;

F) from 0 to about 2 weight percent Al_2O_3;

G) from about 0.5 (.48) to about 0.9 (.92) weight percent Fe_2O_3;

H) from about 0.15 to about 0.33 weight percent FeO;

I) from about 0.1 to about 1.36 weight percent CeO_2; and

J) from about 0.02 to about 0.85 weight percent TiO_2.

Silica forms the glass matrix. Sodium oxide, potassium oxide, magnesium oxide, and calcium oxide act as fluxes to reduce the melting temperature of the glass. Alumina regulates the viscosity of the glass, and prevents divitrification. Moreover, the magnesium oxide, calcium oxide, and alumina act together to improve the durability of the glass. Salt cake or gypsum acts as a refining agent, while carbon is a known reducing agent.

Iron is added, typically as Fe_2O_3, and is partially reduced to FeO. The total amount of iron in the batch is critical, and must equal from 0.7% to about 1.25% by weight, expressed as Fe_2O_3. Likewise, the degree of reduction is critical and must equal between 23% and 29%. The aforementioned critical ranges, for total iron and the degree of reduction from ferric to ferrous iron, result in concentrations from about 0.51 to about 0.96 weight percent Fe_2O_3 and from about 0.15 to about 0.33 weight percent FeO in the glass. If the iron is more highly reduced than the critical amount, the glass will become too dark and the Illuminant A visible light transmittance will drop below 70%. Additionally, the glass batch melting process will become increasingly difficult as the increased amount of FeO prevents the penetration of heat to the interior of the melt. If the iron is less reduced than the critical amount, or if a lower total amount of iron is employed, then the total solar energy transmittance for a desired thickness glass can rise above about 46%. Finally, if an amount of total iron higher than the critical amount is used, less heat will be able to penetrate the interior of the melt, and the batch melting process will become increasingly more difficult. Clearly, the high total iron concentration, and low reduction to FeO, are critical to the performance of the glass, and contrary to the teachings of that prior art directed to glass compositions having a high visible light transmittance and low infrared energy and ultraviolet radiation transmittances.

Moreover, the concentration of the ceric oxide ultraviolet radiation absorber, in concert with the iron, is critical to the balance of transmittance properties. The ceric oxide must be present at a concentration from about 0.2% to about 1.4% by weight. A higher concentration of ceric oxide would absorb more radiation in the 400 to 450 nanometers wavelength range, causing the color of the glass to change from green to yellow-green. A lower concentration of ceric oxide would cause the ultraviolet radiation transmittance to rise above about 38%. A combination of from about 0.1 to about 1.36 weight percent CeO_2 and from about 0.02 to about 0.85 weight percent TiO_2 may be substituted for the aforementioned amount of from about 0.2 to about 1.4 weight percent of ceric oxide alone. The combination of ceric oxide and titanium dioxide have the same operability and utility as the greater required amount of ceric oxide alone, and deviations above or below the stated maximums and minimums for these ingredients will detrimentally affect the absorbence and color properties of the glass as recited hereinabove for ceric oxide alone.

As can be seen, the synergistic effect of the critical concentration limits for the iron and ceric oxide, and the critical limitation for the degree of reduction of Fe_2O_3 to FeO, is to produce a green glass composition having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance of less than about 38%, preferably less than about 34%.

Moreover, the green glass of the present invention is characterized by an Illuminant C dominant wavelength from about 498 to about 525 nanometers, and displays a color purity from about 2% to about 4%. The purity of an automotive vision glazing is an important parameter, and should be maintained at as low a level as practicable. Blue glass, by comparison, has a purity of up to about 10%, and therefore is less desirable as an automotive vision glazing.

As hereinbefore indicated, the invention particularly contemplates and concerns glazings of glass thicknesses in the range of 3 mm to 5 mm. Examples of soda-lime-silica compositions in accordance with the invention at specific thicknesses in this range are set forth below. All of these glasses have Illuminant A visible light transmittances equal to or greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 36%.

Table I

Total Weight % in Glass	3 mm	4 mm	5 mm
Fe_2O_3	.71 to .95	.54 to .65	.51 to .59
FeO	.26 to .32	.18 to .22	.14 to .17
CeO_2	0.8 to 1.4	.55 to 1.2	0.2 to 0.7
% Reduction	23 to 29	23 to 29	23 to 29

Table II

Total Weight % in Glass	3 mm	4 mm	5 mm
Fe_2O_3	0.68 to 0.92	.51 to .62	.48 to .56
FeO	0.26 to 0.32	.18 to .22	.14 to .17
CeO_2	.5 to 1.2	.3 to .75	.1 to .4
TiO_2	.02 to .85	.02 to .45	.02 to .3
% Reduction	23 to 29	23 to 29	23 to 29

Examples 1-16

Typical soda-lime-silica glass batch ingredients were mixed, together with rouge, a cerium compound, a carbonaceous reducing agent, and optionally a titanium compound, and melted to produce 4 mm thick test samples in accordance with the invention. The resultant glass samples are characterized as follows:

Table III

Glass Properties at 4 mm

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Total Iron, as Fe_2O_3 (%)	.782	.789	.783	.788	.788
Reduction of Iron to FeO (%)	25.1	25.7	26.2	27.3	27.5
Fe_2O_3(%)	.586	.586	.578	.573	.571
FeO (%)	.177	.182	.185	.194	.195
CeO_2 (%)	.913	.909	.915	.914	.913
TiO_2 (%)	0	0	0	0	0
Illuminant A (%) Transmittance	72.8	72.3	72.2	71.2	71.5
Total Solar Transmittance (%)	45.9	45.1	44.8	43.9	43.7
UV Transmittance (%)	33.0	33.2	33.3	33.5	33.5
Dominant Wavelength (nm)	512.8	509.2	508.2	505.2	504.5
Color Purity (%)	2.4	2.4	2.5	2.8	2.9

Table III (cont.)

Glass Properties at 4 mm

	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11
Total Iron, as Fe_2O_3 (%)	.784	.78	.78	.84	.81	.833
Reduction of Iron to FeO (%)	27.7	27.4	27.0	25.8	26.7	26.5
Fe_2O_3(%)	.567	.566	.569	.623	.594	.612
FeO (%)	.195	.192	.190	.195	.195	.199
CeO_2 (%)	.911	.6	.6	.91	.56	.915
TiO_2 (%)	0	.2	.2	0	.25	.021
Illuminant A (%) Transmittance	71.6	70.4	70.2	71.5	71.7	71.3
Total Solar Transmittance (%)	43.6	42.9	43.1	43.7	43.8	43.5
UV Transmittance (%)	33.6	30.7	30.1	33.2	33.1	33.4
Dominant Wavelength (nm)	504.6	507.9	507.6	506.5	514.1	505.8
Color Purity (%)	2.9	2.8	2.9	2.6	2.5	2.8

Table III (cont.)

Glass Properties at 4 mm

	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16
Total Iron, as Fe_2O_3 (%)	.813	.84	.74	.74	.85
Reduction of Iron to FeO (%)	26.7	23.0	24.8	28.8	16.4
Fe_2O_3(%)	.596	.647	.556	.527	.711
FeO (%)	.195	.174	.165	.192	.125
CeO_2 (%)	.563	.498	.5	.5	.7
TiO_2 (%)	.253	.25	0	0	0
Illuminant A (%) Transmittance	71.7	71.0	74.2	72	74.9
Total Solar Transmittance (%)	43.8	45.0	47.8	44.3	51.2
UV Transmittance (%)	33.1	33.3	39.4	40.1	28.9
Dominant Wavelength (nm)	514.1	519.0	498.6	495.7	550.8
Color Purity (%)	2.5	2.4	3.3	4.4	4.1

The complete compositions of the glasses of Exs. 11 and 12 are as follows:

	Ex. 11	Ex. 12
SiO_2	71.58	71.64
Na_2O	13.75	13.97
CaO	8.42	8.38
MgO	4.14	3.97
Fe_2O_3	.833	.813
TiO_2	.021	.253
Al_2O_3	.12	.16
SO_3	.13	.14
K_2O	0	.02
Cr_2O_3	.0002	.0003
CeO_2	.915	.563
La_2O_3	.008	.006

Predictive Examples 17-22

	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 22
Total Iron, as Fe_2O_3 (%)	.76	.74	.74	.86	.86	.88
Reduction of Iron to FeO (%)	23	24	23	25	27	26
Fe_2O_3 (%)	.585	.562	.570	.645	.628	.651
FeO (%)	.157	.160	.153	.194	.209	.205
CeO_2 (%)	.2	.3	.4	.5	.6	.7
TiO_2 (%)	0	0	0	0	0	0
Illuminant A (%) Transmittance	70.6	70.6	71.2	71.1	70.0	70.1
Total Solar Transmittance (%)	42.4	42.5	43.3	42.7	41.2	41.1
UV Transmittance (%)	35.2	35.3	34.1	34.4	35.1	32.0
Thickness (mm)	5	5	5	4	4	4

An automotive windshield in accordance with the invention, comprising two sheets of a green glass composition, namely, 71.73% SiO_2, 13.78% Na_2O, 8.64% CaO, 4.00% MgO, .776% total iron expressed as Fe_2O_3 (which is 24.3% reduced to FeO), trace (.017%) TiO_2, .12% Al_2O_3, .14% SO_3, .0003% Cr_2O_3, .89% CeO_2, and .009% La_2O_3, each sheet having a nominal thickness of 2.2 mm, with an interposed polyvinyl butyral interlayer of nominal .030 inch thickness, has the following properties: Illuminate A transmittance = 71.4 %, total solar transmittance = 43.0 %, UV transmittance = 16.3 %, dominant wavelength = 518.6 nm, and color purity = 2.5 %.

A similar automotive windshield in accordance with the invention, consisting of two sheets of a green glass composition including .834% total iron expressed as Fe_2O_3 (which is 26.8% reduced to FeO), trace (.016%) TiO_2, and .913% CeO_2, each sheet having a nominal thickness of 1.8 mm, with an interposed polyvinyl butyral interlayer of nominal .030 thickness, has the following properties: Illuminate A transmittance = 72.2%, total solar transmittance = 44.1%, UV transmittance = 17.1%, dominant wavelength = 511 nm, and color purity = 2.4%.

WHAT IS CLAIMED IS:

1. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from 0.51 to about 0.96 weight percent Fe_2O_3, from about 0.15 to about 0.33 weight percent FeO, and from about 0.2 to about 1.4 weight percent CeO_2.

2. A green-colored glass as defined in claim 1, wherein said weight percent FeO represents a percent reduction of total iron, expressed as Fe_2O_3, of 23% to 29%.

3. A green-colored glass as defined in claim 1, wherein the Illuminant C dominant wavelength is from about 498 to 525 nanometers, and the color purity is from about 2% to about 4%.

4. A green-colored glass as defined in claim 3, wherein said glass at a thickness in the range of from about 3 mm to about 5 mm has an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 38%.

5. A green-colored glass as defined in claim 4, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, the total solar energy transmittance is less than about 45%, and the ultraviolet radiation transmittance is not greater than about 34%.

6. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from .48 to about .92 weight percent Fe_2O_3, from about 0.15 to about 0.33 weight percent FeO, from about 0.1 to about 1.36 weight percent CeO_2, and from about 0.02 to about 0.85 weight percent TiO_2.

7. A green-colored glass according to claim 6, wherein the Illuminant C dominant wavelength is from about 498 to 525 nanometers, and the color purity is from about 2% to about 4%.

8. A green-colored glass as defined in claim 7, wherein said glass at a thickness in the range of from about 3 mm to about 5 mm has an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 38%.

9. A green-colored glass as defined in claim 8, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, the total solar energy transmittance is less than about 45%, and the ultraviolet radiation transmittance is not greater than about 34%.

10. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from about 0.54 to about 0.65 weight percent Fe_2O_3, from about 0.18 to about 0.22 weight percent FeO, and from about 0.55 to about 1.2 weight percent CeO_2, said glass at a nominal thickness of 4 mm having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 36%.

11. A green-colored soda-lime-silica glass as defined in claim 10, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, and the ultraviolet radiation transmittance is not greater than about 34%.

12. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from about 0.71 to about 0.95 weight percent Fe_2O_3, from about 0.26 to about 0.32 weight percent FeO, and from about 0.8 to about 1.4 weight percent CeO_2, said glass at a nominal thickness of 3 mm having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 36%.

13. A green-colored soda-lime-silica glass as defined in claim 12, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, and the ultraviolet radiation transmittance is not greater than about 34%.

14. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from about 0.51 to about 0.59 weight percent Fe_2O_3, from about 0.14 to about 0.17 weight percent FeO, and from about 0.2 to about 0.7 weight percent CeO_2, said glass at a nominal thickness of 5 mm having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 36%.

15. A green-colored soda-lime-silica glass as defined in claim 14, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, and the ultraviolet radiation transmittance is not greater than about 34%.

16. A green-colored, infrared energy and ultraviolet radiation absorbing glass composition, comprising:

A) from about 65 to about 75 weight percent SiO_2;

B) from about 10 to about 15 weight percent Na_2O;

C) from 0 to about 4% weight percent K_2O;

D) from about 1 to about 5 weight percent MgO;

E) from about 5 to about 15 weight percent CaO;

F) from 0 to about 3 weight percent Al_2O_3;

G) from about 0.53 to about 0.96 weight percent Fe_2O_3;

H) from about 0.15 to about 0.33 weight percent FeO; and

I) from about 0.2 to about 1.4 weight percent CeO_2.

17. A green-colored glass composition as defined in claim 16, wherein at thicknesses in the range of 3 mm to 5 mm the Illuminant A visible light transmittance is greater than 70%, the total solar energy transmittance is less than about 46%, the ultraviolet radiation transmittance is less than about 38%, the Illuminant C dominant wavelength is from about 498 to about 525 nanometers, and the color purity is from about 2% to about 4%.

18. A green-colored, infrared energy and ultraviolet radiation absorbing glass composition, consisting essentially of:

A) from about 70 to about 73 weight percent SiO_2;

B) from about 12 to about 14 weight percent Na_2O;

C) from 0 to about 1 weight percent K_2O;

D) from about 3 to about 4 weight percent MgO;

E) from about 6 to about 10 weight percent CaO;

F) from 0 to about 2 weight percent Al_2O_3;

G) from about 0.53 to about 0.96 weight percent Fe_2O_3;

H) from about 0.15 to about 0.33 weight percent FeO; and

I) from about 0.2 to about 1.4 weight percent CeO_2.

19. A green-colored glass composition as defined in claim 18, wherein at thicknesses in the range of 3 mm to 5 mm the Illuminant A visible light transmittance is greater than 70%, the total solar energy transmittance is less than about 46%, the ultraviolet radiation transmittance is less than about 38%, the Illuminant C dominant wavelength is from about 498 to about 525 nanometers, and the color purity is from about 2% to about 4%.

20. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from about .51 to about .62 weight percent Fe_2O_3, from about .18 to about .22 weight percent FeO, from about .3 to about .75 weight percent CeO_2, and about .02 to about .45 weight percent TiO_2, said glass at a nominal thickness of 4 mm having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 36%.

21. A green-colored soda-lime-silica glass as defined in claim 20, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, and the ultraviolet radiation transmittance is not greater than about 34%.

22. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from about .48 to about .56 weight % Fe_2O_3, from about .14 to about .17 weight percent FeO, from about .1 to about .4 weight percent CeO_2, and about .02 to about .35 weight percent TiO_2, said glass at a nominal thickness of 5 mm having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 36%.

23. A green-colored soda-lime-silica glass as defined in claim 22, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, and the ultraviolet radiation transmittance is not greater than about 34%.

24. A green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass including as essential ingredients from about .68 to about .92 weight percent Fe_2O_3, from about .26 to about .32 weight percent FeO, from about .5 to about 1.2 weight percent CeO_2, and about .02 to about .85 weight percent TiO_2, said glass at a nominal thickness of 3 mm having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 36%.

25. A green-colored soda-lime-silica glass as defined in claim 24, wherein the Illuminant C dominant wavelength is from about 498 to about 518 nanometers, the color purity is from about 2% to about 3%, and the ultraviolet radiation transmittance is not greater than about 34%.

26. A green-colored, infrared energy and ultraviolet radiation absorbing glass composition, comprising:

A) from about 65 to about 75 weight percent SiO_2;
B) from about 10 to about 15 weight percent Na_2O;
C) from 0 to about 4% weight percent K_2O;
D) from about 1 to about 5 weight percent MgO;
E) from about 5 to about 15 weight percent CaO;
F) from 0 to about 3 weight percent Al_2O_3;
G) from about 0.5 to about 0.9 weight percent Fe_2O_3;
H) from about 0.15 to about 0.33 weight percent FeO;
I) from about 0.1 to about 1.36 weight percent CeO_2; and
J) from about 0.02 to about 0.85 weight percent TiO_2.

27. A green-colored glass composition as defined in claim 26, wherein at thicknesses in the range of 3 mm to 5 mm the Illuminant A visible light transmittance is greater than 70%, the total solar energy transmittance is less than about 46%, the ultraviolet radiation transmittance is less than about 38%, the Illuminant C dominant wavelength is from about 498 to about 525 nanometers, and the color purity is from about 2% to about 4%.

28. A green-colored, infrared energy and ultraviolet radiation absorbing glass composition, consisting essentially of:

A) from about 70 to about 73 weight percent SiO_2;
B) from about 12 to about 14 weight percent Na_2O;
C) from 0 to about 1 weight percent K_2O;
D) from about 3 to about 4 weight percent MgO;
E) from about 6 to about 10 weight percent CaO;
F) from 0 to about 2 weight percent Al_2O_3;
G) from about 0.5 to about 0.9 weight percent Fe_2O_3;
H) from about 0.15 to about 0.33 weight percent FeO;

I) from about 0.1 to about 1.36 weight percent CeO_2; and

J) from about 0.02 to about 0.85 weight percent TiO_2.

29. A green-colored glass composition as defined in claim 28, wherein at thicknesses in the range of 3 mm to 5 mm the Illuminant A visible light transmittance is greater than 70%, the total solar energy transmittance is less than about 46%, the ultraviolet radiation transmittance is less than about 38%, the Illuminant C dominant wavelength is from about 498 to about 525 nanometers, and the color purity is from about 2% to about 4%.

30. An automotive glazing, comprising a green-colored soda-lime-silica glass containing a high total iron concentration, ceric oxide, and optionally titanium dioxide, said glazing at a thickness in the range of 3 mm to 5 mm having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 38%.

31. An automotive glazing as defined in claim 30, having a nominal thickness of 3 mm, an ultraviolet radiation transmittance less than about 36%, an Illuminant C dominant wavelength from about 498 to about 518 nanometers, and a color purity from about 2% to 3%.

32. An automotive glazing as defined in claim 31, having an ultraviolet radiation transmittance not greater than about 34%.

33. An automotive glazing as defined in claim 30, having a nominal thickness of 4 mm, an ultraviolet radiation transmittance less than about 36%, an Illuminant C dominant wavelength from about 498 to about 518 nanometers, and a color purity from about 2% to 3%.

34. An automotive glazing as defined in claim 30, having a nominal thickness of 5 mm, an ultraviolet radiation transmittance less than about 36%, an Illuminant C dominant wavelength from about 498 to about 518 nanometers, and a color purity from about 2% to 3%.

35. The automotive glazing according to claim 30, wherein said glass is a tempered or heat strengthened float glass sheet.

36. An automotive glazing unit, comprising two sheets of a green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass integrally adhered together through an interposed layer of transparent resinous material, said glass including as essential ingredients from 0.53 to about 0.96 weight percent Fe_2O_3, from about 0.15 to about 0.33 weight percent FeO, and from about 0.2 to about 1.4 weight percent CeO_2, said glazing unit having an Illuminate A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 38%.

37. An automotive glazing unit according to claim 36, wherein each of said glass sheets has a thickness in the range of from about 1.7 mm to 2.5 mm.

38. An automotive glazing unit according to claim 37, wherein said transparent resinous material is polyvinyl butyral.

39. An automotive glazing unit according to claim 38, wherein said polyvinyl butyral layer is about 0.30 inch in thickness.

40. An automotive glazing unit according to claim 39, wherein the Illuminant C dominant wavelength of the unit is from about 498 to 530 nanometers, and the color purity is from about 2% to about 4%.

41. An automotive glazing unit, comprising two sheets of a green-colored, infrared energy and ultraviolet radiation absorbing soda-lime-silica glass integrally adhered together through an interposed layer of transparent resinous material, said glass including as essential ingredients from about 0.5 to about 0.9 weight percent Fe_2O_3, from about 0.15 to about 0.33 weight percent FeO, from about 0.1 to about 1.36 weight percent CeO_2, and from about 0.02 to about 0.85 weight percent TiO_2, said glazing unit having an Illuminant A visible light transmittance greater than 70%, a total solar energy transmittance less than about 46%, and an ultraviolet radiation transmittance less than about 38%.

42. An automotive glazing unit according to claim 41, wherein each of said glass sheets has a thickness in the range of from about 1.7 mm to 2.5 mm.

43. An automotive glazing unit according to claim 42, wherein said transparent resinous material is polyvinyl butyral.

44. An automotive glazing unit according to claim 43, wherein said polyvinyl butyral layer is about 0.30 inch in thickness.

45. An automotive glazing unit according to claim 44, wherein the Illuminant C dominant wavelength of the unit is from about 498 to 530 nanometers, and the color purity is from about 2% to about 4%.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US90/06587

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT CL(5): C03C 3/087, 3/095, 4/08; B32B 17/10, 27/42

U.S.CL.: 501/64, 70, 905

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S	428/337, 339, 426, 437 501/ 64, 70, 905

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	US, A, 4,101,705 (FISCHER ET AL) 18 July 1978 See column 2, lines 29-37 and Examples V and VI.	30-45
Y	US, A, 4,190,452 (FISCHER ET AL) 26 February 1980 See column 2, lines 32-40 and Examples V and VI.	30-45
Y	US, A, 4,701,425 (BAKER ET AL) 20 October 1987 See column 2, lines 31-56.	1-35
X Y	US, A, 4,792,536 (PECORARS ET AL) 20 December 1988 See column 5, lines 10-29 and column 10 lines 44-57	1-36 36-45

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
10 JANUARY 1991	04 FEB 1991
International Searching Authority [1]	**Signature of Authorized Officer** [20]
ISA/US	MARK BELL

Form PCT/ISA/210 (second sheet) (May 1986)